ONTARIO

Ministry of the ENVIRONMENT

Rubber Manufacturing Wastes and Their Effects on Fish and Water Quality

1972

Environment Ontario

RUBBER MANUFACTURING WASTES AND THEIR EFFECTS ON FISH AND WATER QUALITY

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02-003

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SUMMARY

The effluent monitoring program developed by staff of the Ministry of the Environment in co-operation with the Polymer Corporation Limited, encompassed the retention of rainbow trout (*Salmo gairdneri*, Richardson) in the vicinity of waste outfalls and subsequent evaluations of fish flavour, growth and mortality. Supporting chemical and physical data were collected for interpretive purposes.

The data show that both the Polymer Corporation and the upstream refinery and petrochemical plant of Imperial Oil Enterprises Limited, are discharging wastes that taint the flesh and stunt the growth of fish inhabiting waters downstream from their outfalls. The literature on fish tainting and toxicity related to oil refining, petrochemical and rubber manufacturing wastes is found to be largely in agreement with the findings of this project.

INTRODUCTION

During the period July to December, 1971, studies were developed to assess the waste water from the Polymer Corporation Limited (P.C.L.) and its effects on fish and receiving water. Polymer, a crown corporation of the Canadian government is engaged in the production of synthetic rubber.

Continuing efforts by the Polymer Corporation Limited have resulted in major reductions in oil, latex and suspended solids and some reductions in dissolved organic material discharged to the St. Clair River. However, substantial amounts of organic chemicals remain in the waste and information concerning the biological effects of these contaminants was considered a necessary prerequisite to determining the status of pollution control and possible need for additional abatement programs.

A questionnaire survey distributed to water users along the St. Clair system in 1969 indicated that water use and enjoyment was severely limited or stopped by such conditions as floating scums and particles, oil slicks, tainting of fish as well as foul, oily, chemically smelling water (Appendix IV)

DESCRIPTION OF THE STUDY AREA

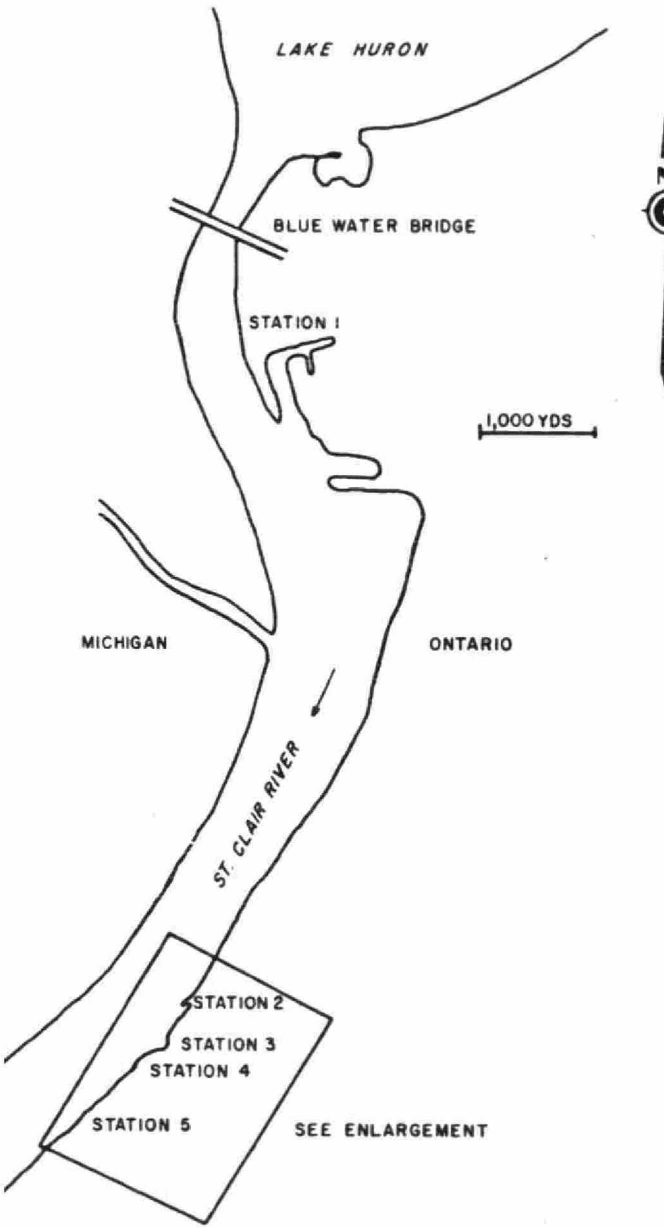
The St. Clair River which receives the Polymer wastes has a mean annual flow of 178,000 cubic feet per second. The river connects Lake Huron on the north with Lake St. Clair, the Detroit River and Lake Erie on the south. Effluents entering the river on the Canadian side upstream of Polymer include the Point Edward sewage treatment plant, the City of Sarnia (population 57,000) primary sewage treatment plant effluent, storm sewers and the waste water from the Imperial Oil Enterprises Limited oil refinery and petrochemical plant. Some downstream effluents include those from Dow Chemical of Canada Limited, Sun Oil Company Limited, the Ethyl Corporation of Canada Limited and Shell Canada Limited. This report deals only with the wastes from the Polymer Corporation but certain observations and conclusions concerning upstream discharges are made.

Dissolved organic wastes discharged by the Polymer Corporation originate from the manufacturing of butyl rubber, stereo specific (e.g. cis-polybutadiene) rubber, co-polymer rubber of styrene and butadiene and a latex form of the co-polymer rubber.

The basic raw materials for the production of monomers which are subsequently polymerized to rubber include benzene purified from crude light oil, ethylene, styrene, butadiene (from butylene) and isobutylene. Other substances used in the process include isoprene, soaps and emulsifiers, acids, talc and salt. Figure 1 outlines diagramatically the major operating units and their related cooling water and process water discharges. The major contaminants and the volume discharge of each of the major sewers are documented in Table 1 and 2 respectively of Appendix 1.

The field program involved retaining fish in five tanks located along the river bank downstream of specified waste discharges. The river water was pumped through the tanks continuously for 12 weeks. Two of the fish tanks (stations 1 and 2) were upstream of the Polymer property and three (stations 3, 4 and 5) were on Polymer property.

Station 1 was a live well owned by a commercial fishing company. Station 2 was located downstream of all discharges entering the river before it passed in front of the Polymer plant. The discharges upstream of this station include the Point Edward sewage treatment plant and storm sewers, the City of Sarnia sewage treatment plant and storm sewers, the Imperial Oil Enterprises Limited pressure sewer, number 5 separator effluent and the separator effluents from combined sewers 9/10 and 11/12. Station 3 was located downstream of a drainage ditch referred to locally and in



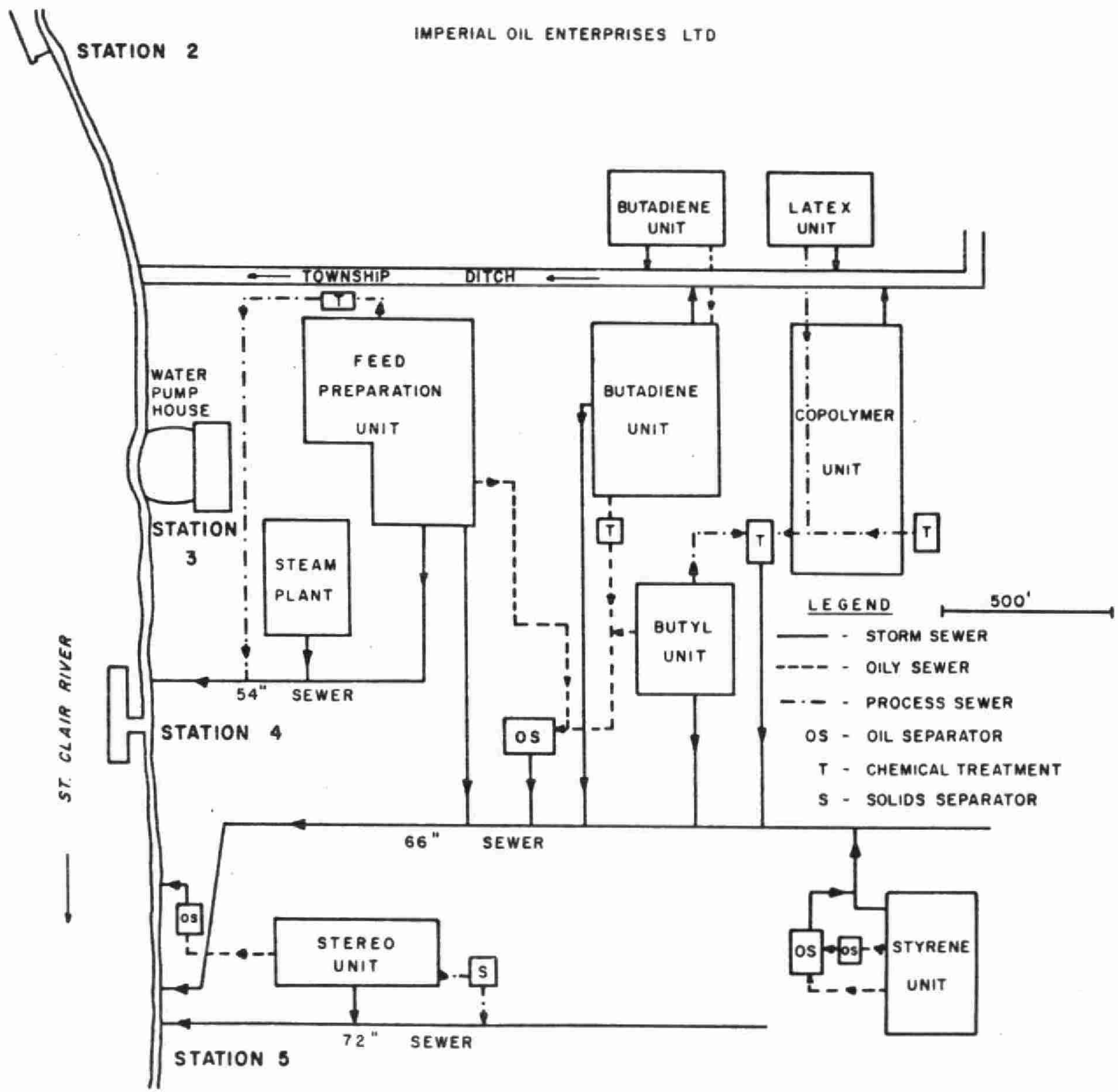


FIGURE 1: STATION SITES AND POLYMER SEWER PLAN

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the report as the township ditch (Highway 40 ditch). Cooling water from the latex unit, butadiene unit, feed preparation unit and the co-polymer unit comprise 95% of the flow in this drainage canal. It should be noted that the water supply pumphouse for the plant is also downstream of the township ditch. Thus, any contamination discharged to the ditch may be drawn back into the plant. The next major discharge downstream is a 54-inch sewer which carries process waste water from the feed preparation unit including the isobutylene plant. In this unit tertiary butyl alcohol is converted, in an acidic medium, to butylene and subsequently dehydrogenated to butadiene. Station 4 was located downstream of the 54-inch sewer.

Waste waters from the dehydrogenation process, the latex unit and the co-polymer unit among others are discharged to a 66-inch sewer which carries the bulk of the contaminated waste water from the plant. The last major outlet is a 72-inch sewer which has a relatively small flow. Station 5 was situated downstream of both the 66-inch and 72-inch sewers.

All of the Polymer sewers discharge at the shoreline.

The total distance from station 1 to 5 is 7000 yards with the last four stations in the lower 1000 yards.

METHODS

Field Studies

Field bioassays were undertaken at the five locations by utilizing 300 gallon plastic exposure tanks supplied with water pumped continuously from the St. Clair River. The pump intakes at all stations were covered with protective trash racks. Fish tanks located at stations 1 and 2 were designed to act as controls on the remaining three locations affected by the wastes from the Polymer Corporation. The intakes for stations 2-5 were determined basically by mechanical logistics but also to allow for some estimation of dilution ratios. The intakes for stations 2 through 5 were located at the downstream boundary of what was considered a reasonable zone of dilution. The fish at stations 2 to 5 were therefore exposed to water containing a relatively high concentration of the discharge immediately upstream and varying but lesser concentrations of all other upstream discharges on that side of the river. The dilutions of the waste waters varied but would be in the order of 2:1 to 10:1 river water to waste water (Appendix 2.)

The average dilution of the township ditch at station 3 would be in the order of 5:1 with a maximum of 9:1. The dilution range of the 54-inch sewer at station 4 ranged from 1:1 to 4:1 with an average dilution of 2:1. The dilution of the 66-inch sewer at station 5 would be between 5:1 and 10:1.

Preliminary, acute toxicity bioassays indicated that grab samples of the township ditch, the 54-inch sewer, the 66-inch sewer and the 72-inch sewer were not toxic to fathead minnows (Pimephales promelas Rafinesque) at 100% in 96 hours so heavy mortality in the fish tanks was not expected.

Rainbow trout (Salmo gairdneri, Richardson) averaging 226 gms in weight were obtained from a hatchery at Normandale operated by the Ministry of Natural Resources. The fish were transported from the hatchery to the exposure tanks in two lots. The first lot was used to stock tanks 1, 4 and 5 while the second lot was used to stock tank 1, 2 and 3.

Aeration on the first transfer was supplied by a battery-driven 12-volt air pump. On the second transfer aeration was provided from a bottle of compressed oxygen. To reduce any bacterial or fungal diseases during the crowded conditions of transfer, each 75-gallon tank was treated with 12 x 250 mg capsules (9.4 mg/l) of tetracycline.

Once the experiment was underway a daily inspection included cleaning and adjustment of all mechanical components, measurements of temperature, dissolved oxygen (Winkler) and pH and observations on the general health, vigor and feeding behaviour of the fish. Since the experiment was intended to run for 12 weeks the fish were sampled for taste testing at six weeks and again at the end of the exposure period.

Water samples for chemical and threshold odour analysis were also collected. The fish were fed a common diet until satisfied on five occasions per week.

Laboratory methods - Taste Testing

Fish used in the flavour evaluation studies were taken from the exposure tanks, sacrificed, weighed and measured, and then frozen in an ice chest with dry ice. On occasions when fish were killed by batches of toxic waste (October 17, November 8, November 27) they were frozen as soon as they were discovered and weight and length recorded at a later date. On arrival at the laboratory, fish were held in a deep freeze until the day before the test, at which time they were transferred to a cold room. After approximately 16 hours in the cold room the fish were still frozen but softened sufficiently to be prepared for taste testing.

Preparation of samples

Six samples from each fish, each of approximately one cubic inch were taken from fillets cut from the meatiest part of the fish between the dorsal and lateral line.

Skin and large bones were removed. The samples were placed in new, aluminum foil baking cups, covered tightly with pieces of aluminum foil and assigned numbers in a coded sequence known only to the author.

Samples prepared in this manner were then refrigerated until required in the test. Cups of fish were placed on enamelled trays and baked for 15 minutes at $300^{\circ}F$. The samples were then taken to the test room where they were kept warm under a heat lamp for a maximum of twenty minutes.

Taste Panel

The personnel pool of 11 people for the taste panel consisted of staff from the Ministry of the Environment, Water Quality Branch and Laboratories Branch and the Polymer Corporation. These people professed no dislike for fish and were able to attend the tasting sessions regularly.

Taste Tests

The tasting sessions were held, two per day, in an unoccupied air-conditioned room on October 6, 7 and 8 and December 8, 9 and 10, 1971. The sessions were scheduled an hour after meals. Panelists were asked to refrain from smoking prior to tests. Women judges were asked to remove their lipstick and all panelists washed their hands with odour-free soap before each test session. All glassware and implements had been washed with odour-free soap and rinsed with distilled water.

Each panelist was provided with an individual "place-setting" consisting of a dish of unsalted crackers, waste container, fresh paper cup, flask of rinse water and instruction

sheet. Rinse water was made by adding 1 tablespoon of lemon juice to 1 litre of distilled, deodorized water.

For each session the judges were presented with a series of samples two at a time identified only by number. They were instructed to smell and note for future reference the steam from each of the freshly opened, warm samples. Judges were asked to taste the fish, deposit the chewed portion of fish in a waste beaker, chew a cracker and rinse the mouth with the diluted lemon juice and place all waste in the containers. The numbered samples were tasted in turn with a cracker chewed and the mouth rinsed between each sample. The presence or absence of foreign flavour was recorded as follows:-

1 - absent

2 - barely perceptible

3 - definite

4 - strong

Threshold Odour Tests

Threshold odour tests were carried out on various river and waste water samples during the time the fish were retained in outfall areas. The odour tests, run at both 40°C and 60°C were performed according to "Standard Methods for the Examination of Water & Wastewater", 13th ed.

Total Fat Content of Fish (Benzene extract)

Fat contents of the fish were measured in an attempt to assess the general health and vigor of the fish. A small portion of meat was taken from each fish, ventral to the lateral line and immediately posterior to the pectoral girdle, homogenized and analysed for fat content using a benzene extraction technique. Sampling fish in this manner reduces the variability that may be introduced due to differing fat concentrations at different sites within the body of the fish.

The numerical data obtained from these procedures were analysed using a Chi-square test. In the results of the taste tests, experimental stations (stations 3,4,5) were compared for total positive and definite-strong responses against the two control stations (stations 1 and 2.) Such a comparison was made for the 40 and 80 day exposure. A similar statistical comparison of average fish weights and fat content was made after 40 and 80 days exposure.

RESULTS

Field Studies - Station 1

Fifty-two rainbow trout were stocked at this station on September 15 (Appendix 1, Table 3). One fish died on September 18 and from that date to October 25 there was no mortality or apparent disease. On September 23 a total of 50 trout were transferred from this tank; 30 to station 4 and 20 to station 5. Forty replacement fish were added to station 1 on September 24. Changes in the fish populations of the various stations are indicated in Table 3 as a series of time lines. From September 18 to December 6 there were no mortalities and few diseases of fish at this station. Twelve trout were removed on October 25 for taste testing, 15 on October 28 for partial restocking of staion 5, and a final 12 on December 6 for taste testing.

On November 20 and 21 a strong north-west wind reduced the clarity of the river water. Consequently, the tank could not be properly cleaned or the fish accurately counted or observed until the experiment was terminated on December 6. During the period of November 22 to December 6 the rate of feeding of fish was unknown.

The usual condition of the water at this station can be described as clear, odour free and well oxygenated (Appendix 1, Table 5). Fish at this station fed vigourously throughout the experiment although this cannot be substantiated for the period November 22 to December 6 when water conditions prevented observation.

Station 2

Thirty rainbow trout were put into the tank on September 15. One fish died on September 19 from unknown causes and another on September 25 probably from fin rot. No signs of disease were evident on another trout that died on September 30. Early in October an estimated seven trout were lost to poachers. On October 25, twelve fish were removed for taste testing leaving a balance of eight fish. A power failure in the Imperial Oil Refinery on the afternoon of October 28 resulted in a great deal of oil and, what was described as coke dust, being discharged to the river. The brown dust appeared about two hours after the power failure in all the downstream tanks. These unusual discharges from Imperial Oil had no obvious effect on the fish. On November 22 the water in this tank became very cloudy for the reasons noted previously. This turbidity, which prevented adequate cleaning of the tank and counting of the fish, persisted until the experiment was terminated on December 6. On December 6 the remaining eight trout, one of which had recently died were sampled.

Conditions at this station were influenced by ambient river temperatures and pH's. The water was well saturated with oxygen at all times (Appendix 1, Table 5). The river at this station and to a lesser extent the fish tank itself, had a permanent oil slick. Large quantities of sewage fungus were regularly cleaned from the trash rack around the pump intake and

fungus and algae from inside the tank. Ten days exposure to the water of this station was sufficient for the fish to show a marked reduction in feeding. The river water possessed a chronic sour, sulphurous, oily smell.

Station 3

Twenty-seven rainbow trout were put into this tank on September 13 and an additional three on September 15. The water at this station was generally clear and well-oxygenated and temperature and pH levels were characteristic of the river. Appendix 1, Table 5. Occasionally, small particles of oil could be seen floating in the tank. Generally, the fish responded well to feeding. No mortality occurred and only a very low incidence of disease was evident.

In describing the behaviour of the river and the effluent stream at this station certain important features must be noted. The momentum of the water coming out of the township ditch tended to push the oil slick coming down the river out from the shore. As the river moved past the pumphouse (Figure 1) a back eddy was formed which pulled the plume from the township ditch back into shore where the water was drawn past the fish tank intake and into the fore bay of the pumphouse. Field observations indicated that material leaving the township ditch appears in the fore bay of the pumphouse in about 5 minutes.

Station 4

Unlike the previous three sites, experimental conditions at this station were complex and varied as a result

of malfunctioning equipment and an unpredictable and often lethal effluent. For reasons of industrial safety an explosion-proof motor had to be used at this site and since the associated pump was not suitably designed for this application flow volumes through the tank were highly erratic.

Thirty rainbow trout were put into this tank on September 15. The water temperature at the hatchery was 15°C while that of the exposure tank was 24°C. Twenty pounds of ice were added to lower the water temperature but despite this precautionary measure the temperature rose 9°C. From September 15-21 inclusive 18 fish died. Ten trout remained in the tank and so 30 more were added on September 23 from extra stock held at station 1. No further mortality was noted from September 23 to October 3 inclusive although the fish demonstrated poor appetite during this period. Through the ensuing weeks there was an unending series of severe pH fluctuations, pump failures and intentional pump shutdowns to protect the fish from the lethal effluents. The extremes of pH measured in the river at the pump intake were 2.6 - 12.5 (Appendix 1, Table 5).

The trout that died on October 4 and a number of the survivors had moderate to severe skin lesions, which had first been noted on September 20. These lesions would begin as a localized roughening of the epidermis followed by sloughing of the scales and skin. When these lesions occurred on the dorsal half of the fish the underlying muscle layers could be clearly

seen. Lesions on the ventral half of the fish frequently penetrated the body wall exposing the body cavity and internal organs. On October 8 about half the fish showed lesions but after a few days many of these were healing and the incidence of this malady gradually disappeared. None of the fish in the other tanks showed a similar skin condition or pattern of mortality.

Operating records of the Polymer Corporation indicate that the isobutylene plant was shut down for repairs from November 1-5. During this period there was virtually no waste water coming from this area. Field records indicate that prior to and following this period the fish were feeding poorly but from November 1-5 they were feeding very well. Thus, there would appear to be a good co-relation between the depressed feeding activity of the fish and the operation of the isobutylene plant.

From November 6-22 no mortality or disease was noted although the pH of 54-inch sewer showed wide fluctuations. After November 22nd excessive turbidity prevented adequate checks on the numbers or condition of the fish. On November 27 the remaining six fish in this tank were killed by an extreme, alkaline (12.5) pH (Table 4.). These fish were subsequently used in flavour evaluations.

Station 5

This station went into operation on September 13. Four days after stocking a major machanical failure in the

fish tank pumping system led to the death of all fish. Necessary repairs were completed and the tank was restocked with 20 trout on September 23 and an additional ten on September 24. All fish survived the restocking and appeared in good condition.

From September 27 to October 17 there was no mortality or apparent disease in any of the fish. Throughout this period the fish were feeding satisfactorily but on October 17 the entire stock was killed by a lethal discharge (Appendix 3.)

This tank was subsequently restocked with 15 trout on October 28. Apart from one fish which apparently jumped out of the tank all remaining fish fed well and survived the experimental condition with only a very slight incidence of disease. On November 8 all fish were killed by another lethal discharge.

Spills and Unusual Discharges

Table 4 of Appendix 1 summarizes some of the major and minor spills and slug discharges at stations 4 and 5. Of the 19 incidents listed five were detected through visible changes in the effluent, another five were detected through resulting fish kills, eight were detected through pH monitoring and one (December 7) through other manifestations.

The spills and unusual discharges noted at station 4

were shown by extreme fluctuations in pH and the occasional fish kill when preventive, protective action was not taken. These pH disturbances arose exclusively in the feed preparation area. At station 5 discharges from the styrene unit predominated in frequency and severity. Other units contributing to spills observed at this station were the stereo unit, butyl unit, butadiene unit and the copolymer unit.

On November 8 a mixture of styrene, benzene and ethyl benzene was discharged from the styrene unit to the 66-inch sewer. This discharge which lasted less than one hour resulted in the death of all fish at station 5. There was no damage to a polystyrene float supporting the water intake for this station. On December 7 a discharge of 1,100 gallons of similar material resulted in extensive dissolution and melting of the float. Styrene and ethyl benzene were measured in the 66-inch sewer at 250 ppm and 80 ppm respectively. An analysis for benzene was completed but none detected.

Table 4 illustrates that under conditions of frequent observation more than 30% of the observed incidents resulted in dead fish. This value would have been much higher if preventive action had not been taken repeatedly at station 4. Such action included shutting off the water supply pump and adding fresh, domestic water or oxygen to the liquid in the tank.

Laboratory Studies - Chi-Square Definition

The Chi-Square test was used to determine if any of the differencesbetween the control fish (expected frequency) and the experimental fish (observed frequency) were significant. The Chi-Square test is based on the null hypotheses that there is no difference between the observed frequency or measurement and the expected frequency or measurement. If the Chi-Square calculation indicates a difference between the two groups of data then the size of the difference determines the degree of confidence that can be placed in the results. If the difference is large then there is a greater certainty that the observed difference has arisen from the defined, experimental conditions and not from random variation between the two groups.

Fish Tainting

A total of 600 samples taken from 100 fish were prepared for taste testing. The results of the evaluations are included in Table 1.

Fish flavour evaluation studies indicated that after 40 days of exposure to the water of the St. Clair River the fish of station 1 were not tainted while those of stations 2,3 and 4 were definitely/strongly tainted to the 99.9% level of confidence (Table 1). Similarly, after 80 days of exposure the fish of station 1 were not tainted while those of stations 2,3 and 4 were definitely/strong tainted to the 99.9% confidence level. The trout of station 5 were definitely/strongly tainted

Table 1: Incidence of foreign flavour in rainbow trout samples. 40 day exposure.

Station	# of Samples	FOREIGN FLAVOUR 1	2	3	4	TOTAL Pos.	Definite Strong
1	72	58	13	1	0	14	1
	% 100	81	18	1	0	19	1
2	72	0	5	24	43	72	67
	% 100	0	7	33	60	100	93 *
3	72	6	8	34	24	66	58
	% 100	8	12	47	33	92	80 *
4	72	0	4	11	57	72	59
	% 100	0	5	16	79	100	95 *
5	30	0	0	4	26	30	30
	% 100	0	0	13	87	100	100 *
	36	0	1	12	23	36	35
	% 100	0	3	33	64	100	97 *

* Results significantly different from the controls at the 99.9% confidence level.

80 day exposure

Station	# of Samples	1	2	3	4	Pos.	Definite Strong
1	72	62	8	2	0	10	2
	% 100	86	12	2	0	14	2
2	48	1	12	14	21	47	35
	% 100	2	25	29	44	98	73 *
3	102	6	34	35	27	96	62
	% 100	6	33	34	27	94	61 *
4	24	1	6	8	9	23	17
	% 100	4	25	33	38	96	71 *

* Results significantly different from the controls at the 99.9% confidence level.

at a confidence level of 99.9% after 11 and 23 days.

Chi-square analyses show no significant difference between the 40 and 80 day exposure for stations 2, 3 or 4 or the 11 day and 23 day exposure for station 5.

Using station 2 as a control for stations 3, 4 and 5 there is no significant difference in the intensity of tainting between these stations.

Assuming that two-thirds of the samples from a fish must be rated as having a definite-strong unnatural flavour before that animal would be considered as tainted, then Table 2 indicates the percentage of fish that would be rated as tainted after 11, 23 and 40 and 80 days of exposure at each station.

On a qualitative basis the flavour of the fish at station 1 was described by panelists as bland and fish-like with a distinctive, flaky texture. The raw fish had a pleasant, mild fish-like odour. Uncooked fish from station 2 and 3 had a sulphurous, cabbagey, mercaptan-like, oily odour while the cooked fish tasted predominently of oil or gasoline. Using an analysis of variance to compare the intensity of tainting at stations 2 and 3 the ratings of the taste panel indicated that the intensity of the tainting at the latter was significantly less than the former. The raw fish from station 4 had a very distinctive odour resembling tertiary butyl alcohol. The cooked fish had a flavour similar to those from station 2.

At station 5 two distinct types of aroma in the raw fish and flavour in the cooked fish were noted. One group of fish from this station smelled and tasted of a reduced hydrocarbon (likely styrene) while the other group of fish had an oily odour resembling that of quench oil and a rubbery taste. After the fish of the first group had been standing in the open air for several hours the styrene-like odour was lost and the fish took on an oily aroma similar to that of quench oil.

Another phenomenon that was noticed was that the fish of stations 2 and 3 lost the sulphurous odour on cooking. Cooking also removed the garlic-like odour of tertiary butyl alcohol associated with the fish of station 4. These changes rendered the presumably less volatile, oily gasoline-like odours more evident.

Table 2: Percentage of tainted fish per station (see text).

Station	Duration of Exposure			
	11 days	23 days	40 days	80 days
1			0%	0%
2			100%	75%
3			92%	59%
4			100%	75%
5	100%	100%		

Laboratory Studies - Fish Weight and Fat Content

Table 3 presents the average weight of the fish at various locations with increasing exposure time. It can be seen that fish from station 1 gained weight significantly while those of station 2 lost weight. Compared with their starting weights the fish from stations 3 and 4 did not change significantly during the 80 days. Owing to the impact of recurring lethal discharges necessitating replacement of fish it is felt that any weight differences noted in the fish of station 5 would not be a reliable index of their growth.

Comparing mean weights of control fish to the mean weights of fish from stations 2, 3 and 4, the control fish were significantly heavier after 40 and 80 days exposure. Using the Chi-squared test of comparison and station 2 as a control against stations 3 and 4, the fish from station 3 were significantly heavier than the controls (station 2) but those from station 4 were not. Similarly, at 80 days exposure the fish of station 3 were significantly heavier than the controls (station 2) whereas fish from station 4 were not. These differences were due to the fact that the fish from station 3 grew slightly whereas the fish from station 2 lost weight, thereby increasing the difference between the two stations. The fish from station 4 lost weight thus minimizing any difference between station 2 (control) and station 4.

It can be seen from Table 3 that the changes in weight of the fish and their fat content are rising and falling in a parallel manner and that this pattern is the same as has been noted for the intensity of tainting (Table 5) and the feeding activity of the fish.

TABLE 3: Mean Weight of fish (gms) and fat content % w/w at each station vs. duration of exposure.

STATION	0	11			23			40			80		
		N	$\bar{x}$ wgt.	% Fat	N	$\bar{x}$ wgt.	% Fat	N	$\bar{x}$ wgt.	% Fat	N	$\bar{x}$ wgt.	% Fat
1	226**							12	284	2.7	12	343*	2.3
2	226**							12	212	2.0	8	194*	1.2
3	226**							12	243	2.2	2.0	245**	2.9
4	226**							12	211	1.7	6	213	1.8
5	226**				14	228	1.9						
	284	28	240	2.7									

* Weight changes significantly different from starting weight at the 95% confidence level.

+ Weights significantly different from those of station 2 at the 95% confidence level.

** Average weight of fish based upon an estimate of the hatchery population.

N Equals the number of fish measured at the end of each exposure period.

Laboratory Studies - Threshold Odour and Chemical Analysis

The river and waste streams related to this study were sampled for threshold odour determination and various chemical parameters.

The samples were collected shortly before the fish were to be sampled for subsequent taste tests. Table 4 contains both the threshold odour values and comments concerning the types of odour found and indicates that as far down the river as the Imperial Oil Refinery the shore line water is relatively free of odourous materials. After the refinery wastes are discharged to the river the threshold odour number (T.O.N.) increases from approximately 10 to 1000. The table also indicates that the odour of wastes in the combined sewer serving separators 11/12 was higher than all other samples. There was also a change in the quality of the odour. The uncontaminated river has a fish-like or vegetation-like odour while below the Imperial Oil outfalls the odour is described as cabbage, garlic, petroleum oil.

The township ditch, which contained almost exclusively (95%) cooling water from P.C.L. has a relatively low threshold odour. The threshold odour intensity of the township ditch water was generally less than its source water which was equivalent to the water in the fish tank of station 3. The implication here is that as the water moved through various heat exchangers to provide cooling functions some of the odourous components were lost.

The threshold odour values of station 4 were in the order of 1100. The aroma of butyl alcohol was named as one of the odours present in the sample. It was also noted that the odour causing material was very volatile.

Table 4: CHEMICAL ANALYSIS OF THE ST. CLAIR RIVER

Station	PARAMETER S= ppm	B.O.D. ppm	C.O.D. ppm	pH	NH_4 ppm	Phenol ppb	T.O.N. 60 °C	Description
1	0	0.4	<30	7.6	0.02	2	27	Weedy, fishy, acid vegetatio
Above I.O.E.L 9/10	0	0.8	<30	8.1	0.01	8	15	Mildew, Rubber, oily
I.O.E.L. 9/10	0	19	35	8.9	0.19	60	2141	Oily, rubbery, gasoline
I.O.E.L. 11/12	5	160	550	9.5	1.1	65	35,350	Cabbage, oily, petroleum
2	-	3	<30	7.9	0.08	-	1778	Cabbage, acetylenic, oil
Twp. Ditch	-	4	<30	7.8	0.20	10	89	Oily, rubbery
3	-	4	<10	8.3	0.10	10	20	Oily, weedy, rubbery
54" sewer	-	10	350	8.3	0.40	8	1379	Paint, Plastic, Butyl Alchol
4	-	12	95	8.1	0.2	-	1148	Oily, garlic, septic, musty
66" sewer	0	40	80	8.9	2.6	108	2125	Oily, Kerosine, acetylenic
72" sewer	-	5	50	7.1	0.1	130	24	Chlorine, oily
5	-	12	65	8.1	0.5	-	1075	Chlorine, acetylenic, turpentine

The threshold odour at station 5 was just slightly less than that of station 4. Verbalization on the types of odour present indicated that petrochemical odours predominated along with the odours of reduced sulphur compounds.

It can be seen in Table 8 that there is a general increase in B.O.D., C.O.D., ammonia and threshold odour from station 1 through 5. These parameters are indicative of the increasing pollutional load carried by the river.

DISCUSSION

The St. Clair River between Lake Huron and the upstream limits of the Imperial Oil outfalls was shown to be relatively odour free. Based upon many field observations at station 1 the water quality is entirely suited to the maintenance of a healthy aquatic flora and fauna.

At station 2 there has been a rapid deterioration of water quality. The water at this station had a strong odour and a capacity to taint fish and to stunt their growth. Oil slicks are a constant feature of the river at this location. Although all measurements and observations were made from the shore, oil slicks could be frequently seen up to 200 feet off shore. As would be expected the slicks widened with passage downstream. In examining the response cards of the odour panel, descriptive terms such as cabbagey or rotten cabbage (i.e. reduced sulphur compounds) were applied consistently to Imperial Oil combined sewers 11/12. Sewers 9/10 combined were described as oily or gasoline-like. The water at station 2 smelled of oil and reduced sulphur compounds while

the fish tasted of oil. Fish growth rates at this station were severly inhibited and were reflected in the fat contents of the fish which were significantly less than those of the control fish. The multi-purpose usefulness of the water at station 2 has been considerably reduced. The river, at this point, is not suitable for potable water supplies or fish propagation.

While the fish from station 3 fed well, weight increase on the 80-day exposure period was negligible by comparison with station 1 but significantly more than station 2. From a summation of all the observations at station 3, it can be postulated that the badly tainted water coming down the river is drawn through the forebay of the pumphouse and subsequently through various inplant cooling devices. After warming, some of this water is discharged through the township ditch from which it flows downstream to constitute about 20% of the water in the tank at station 3. Detainting, which might occur during pumping, cooling and movement of water through the township ditch would help to explain the generally healthier condition of the fish in station 3 as compared with those of station 2. Another factor, probably of greater importance, is the additional dilution, mixing, volatilization and digestion of Imperial Oil wastes provided by the river between station 2 and 3. Such dilution and assimilation of the refinery waste products is indicated by the fact that the sulphurous odours, so dominating at station 2, are almost entirely absent at station 3.

In view of the distance downstream from Imperial Oil and the results from station 3, it would seem reasonable to attribute tainting of the fish at station 4 less to the

Imperial Oil's effluents and more to the immediate upstream Polymer effluent. If uncontaminated cooling water has less odour than the incoming water at the pumphouse then more of the fish tainting can be attributed to P.C.L. process wastes since the influence of Imperial Oil effluents had diminished considerably.

The water and raw fish at station 4 smelled of tertiary butyl alcohol. The cooked fish tasted of oil.

Throughout the exposure period at this station one of the most notable feature was the lack of feeding on the part of the fish. Food pellets offered to the fish were almost totally ignored. By contrast, a handful of pellets offered to the fish at station 1 would rarely reach the bottom of the tank. The lack of feeding at station 4 continued uninterrupted through periods when the pH of the 54" sewer maintained at steady, near normal levels. The only time the fish at this station showed any interest in the feeding was for a five day period (November 1-5) when the isobutylene plant was not operating and no process waste was being discharged to the sewer. The pH of the water in the fish tank at this time was at ambient river levels. Since the fish showed total indifference to the food pellets on which they had been raised they did not gain weight. Indeed, there was a loss of fat from the tissues of the fish indicating that they were living off energy reserves and would ultimately starve to death.

Another feature of the effluent monitored at this station were the extreme fluctuations in pH. At times, these fluctuations could be anticipated by the plant operating staff and preventive action taken to protect the fish. However, there were repeated incidents where the pH fluctuations were neither anticipated nor controlled and these incidents lead to severe distress and/or death of the fish. Once the lethality of these pH fluctuations was fully appreciated the company made several attempts at

modifying the pH control equipment to reduce the amplitude of the oscillations. These attempts had little effect as indicated by the events of November 27, when the remaining fish at this station were killed by a pH of 12.5.

The fish from station 5 showed two distinct types of tainting. One of these was of an oily, rubbery nature and was noted after 23 days exposure at this station. The other type of taint was similar to a reduced hydrocarbon which smelled, in the raw fish, much like styrene. This second taint was noted after 11 days exposure.

These two groups of fish were the victims of two fish kills observed at this station. The first fish kill (23 days exposure) resulted from the draining of highly contaminated water in the sump from a crude benzene storage tank. The second fish kill (11 days exposure) resulted from a discharge, lasting less than one hour, of a mixture of styrene, ethyl benzene and benzene. Upon exposure to the air after thawing this second group of fish quickly lost the styrene-like odour and took on an odour of quench oil similar to the first group.

These findings indicate that some slug discharges have the capability to both kill fish and severely taint them. Other discharges appear to be lethal without necessarily tainting the fish.

On December 7, a discharge of styrene, ethyl benzene and benzene caused extensive damage to a polystyrene float in the river at the site of the water intake of the dismantled fish tank. Had the fish tank been in operation this discharge presumably would have caused another fish kill. Using a dilution ratio of 7:1 as indicated in Appendix 2, this discharge of 250 ppm styrene and 80 ppm ethyl benzene would have resulted

in approximately 36 ppm styrene and 11 ppm ethyl benzene in the fish tank. An assessment of fish growth could not be made because of these recurring lethal discharges.

These studies indicate that on a numberical basis there is severe tainting at station 2 and less tainting at station 3; stations 4 and 5 are equally and badly tainted when compared to station 1. There is little difference in the intensity of tainting between 40 and 80 days exposure at stations 2, 3 or 4. The fish from station 5 were severly tainted after as little as 11 days exposure. While there are similarities between the stations as far as the intensity of flavor is concerned, there are definite differences as far as the type or quality of flavor is concerned.

In reviewing the different parameters measured at the different stations there is a consistantly recurring phenomenon. At station 1 threshold odour is low, the incidence of tainting is low, the weight gains are high and the fat content is high. Station 2 shows exactly the opposite condition of station 1; odour is high, tainting is high, weight gains are non-existant and fat content is low. Station 3 shows these parameters moving back toward the levels of station 1 and at station 4 there is a relapse back to a condition resembling that of station 2. Station 5 has many features in common with station 2 with the additional, superimposed feature of repeated lethal discharges. All these features are different facets of a larger problem, and that is one of toxic concentrations of dissolved organics discharged to the river.

LITERATURE REVIEW

The fact that fish can acquire unusual flavours or taints from the water has been demonstrated by Thaysen and Pentelow (1935). In this study it was found that, "Certain types of *Actinomyces* produce a pungent odour which has frequently been described as earthy". The contamination of the river under investigation was restricted to the tidal portion where the organic matter was abundant. His studies established that the taint appears to be acquired through the gills and to be carried in the blood stream although uptake through the gut was not discounted. A definite taint could be picked up by the fish in a few hours when they were exposed to tainted water but more than twenty-four hours in clean water was required before there was a noticeable drop in the flavour intensity.

Various authors have alluded to the fact that certain industrial wastes can impart tastes and odours to water and fish (Buswell, 1955; Boëtius, 1954; Diehl, Denbo, Bhatla and Sitman, 1971).

Fetterolf (1964) suggests four avenues by which water borne substances may taint fish. These are:

1. uptake through the gills and into the blood
2. uptake through the gut and into the blood
3. absorbtion through the skin
4. adsorbtion to the mucosa

Fetterolf concluded that uptake of tainting substances through the gills is the most likely route but he does not discount the possibility of uptake through the gut from tainted food.

Nitta _et_. _al_. (1965) concluded that offensive odours were imparted to fish via the gills and circulatory system when oily substances were present in the water at concentrations as low as 0.01 mg/l or as low as 0.2 percent (as ether extracts) in bottom muds. Fish did not avoid water masses containing the odour producing petrochemicals.

Ruchhoft, Middleton, Braus and Rosen (1954) in discussing oil refinery effluents concluded that, "Neutral materials, largely aliphatic and aromatic hydrocarbons were most significant in terms of their taste and odour causing potential and their great persistance and stability in terms of purification processes".

They also noted that phenolic compounds are significant in problems of taste and odour.

In one of the more thorough examinations of fish tainting and oil refinery wastes, Krishnaswami and Kupchanko (1969) established that rainbow trout would acquire an oily taste when held for 24 hours in oil refinery waste which had a calculated threshold odour number of more than 0.25. The degree of in-plant treatment to which these wastes had been subjected was not defined but some of them had apparently been through at least an A.P.I. separator.

After a detailed examination of a large oil refinery Diehl _et_. _al_. (1971) concluded that, "The barometric condensers on the vacuum distillation towers at the pipe stills accounted for almost 50 percent of the odour in the refinery effluent". A number of techniques including detention, activated carbon and bio-oxidation were found to be effective in reducing the odour of the effluent. However, actual odour intensities before and after treatment were not given.

In a study of seven oil refineries Kendall and Neilson (1964) discussed two dominant and two subsidiary types

of odour common to refineries. The two dominant odours are those associated with sulphur containing compounds (sulphides, thiols, thioethers) and those associated with hydrocarbon compounds (kerosene, fuel oil). The subsidiary odours are those producing a burnt odour (creosote) and those producing a pungent reaction or irritation of the olfactory nerve endings. Kendall _et. al_. also demonstrated that various types of bio-oxidation were effective in reducing the odour of refinery effluents but that substantial dilution with odour free receiving water was still necessary to dilute the effluent to the 'recognition level'. The recognition level as defined by Kendall is 2 to 10 times the threshold level. In comparing the work of Kendall _et_. _al_. & Krishnaswami _et_. _al_. it would seem that after bio-oxidation further receiving water dilution of at least 1,000 - 10,000 would still be required to avoid fish tainting.

In examing the toxicity of oil refinery effluents to fish, a number of studies have compared the relative susceptability of various species. (Dorris, Gould and Jenkins, 1959; Douglas and Irwin, 1962; Irwin, 1965). These writers established that the 96-hour TLm is in the order of 15% v/v for most oil refinery effluents. Hardy, resistant species (_Libestes_ _reticulatus_) show a TLm-96 in excess of 25% v/v while a susceptible species (Salmo _gairdneri_) would show a TLm-96 of 11% v/v on the same effluent. Dorris _et_, _al_. (1959) have shown that when a refinery effluent has been treated to be non-toxic at 100% in 48 hours to fathead minnows there is a parallel decrease in immediate dissolved oxygen demand, phenol, sulphide, ammonia, B.O.D. and C.O.D. Jenkins (1964) reached the same conclusion but went on to state that, "No consistent relationship could be demonstrated between toxicity and chemical oxygen demand or alkalinity".

In studying the long term effects of oil refinery wastes on fish, Graham and Dorris (1968) concluded that "Chronic or cumulative toxication occurred during prolonged exposure with treated refinery effluents having no acute toxicity. The dilution reation required to prevent chronic toxication in such effluents appeared to be at least 1:4".

Effluent treatment in the study described by Dorris et. al. consisted of passing the wastes through an A.P.I. separator and then eithor lagooning or passage through a long, open ditch. In the study by Douglas et. al. in-plant or external waste treatment was not specified beyong the statement that the waste was ponded before discharge. In Irwin's study the type of treatment afforded the waste was not specified nor where any chemical parameters given. In his study Jenkins examined 11 different refineries utilizing a wide variety of waste treatment techniques. In the study by Graham et. al. the four oil refineries examined utilized a variety of treatment techniques some of which were relatively simple and discharged a highly toxic waste and others which were somewhat more sophisticated and discharged a waste with no apparent acute toxicity. Graham et. al. also noted the loss of appetite and weight in fish exposed to refinery effluents.

The tainting of fish by organic wastes is well established in the literature. Brandt (1946) states that, "In the waste water from synthetic rubber factories the taste-producing substances are the higher, partially unsaturated, aldehydes and unsaturated hydro-carbons; styrol, in spite of its low solubility imparts taste to fish-flesh". Styrene is soluble in water to about 32 ppm. Rosen et. al. (1963) calculated the threshold odour number of ethyl benzene and styrene to be 7.1 million and 27 million respectively.

Rosen et. al. (1963) reiterates the odour potentiation of complex mixtures of organic chemicals while Klein (1962) noted that "Mixed wastes appear to affect the taste of fish more than simple compounds", and that three to five parts per million of coke oven waste (roughly equivalent to the tank drainings causing the first fish kill at station 5) had been found to be lethal to fresh water fish. In discussing the toxicity of various waste components of synthetic rubber manufacturing, Trvelle (1958) considered styrene and ethyl benzene to be the most lethal.

Pickering and Henderson (1966) in discussing the acute toxicity of some important petrochemicals to fish indicated that styrene, ethyl benzene and benzene have 24-hour TLms to fathead minnows (Pimephales promelas, Rafinesque) on soft water of 56.73 mg/l, 18.51 mg/l and 35.56 mg/l respectively. In discussing the same topic Zelinka (1957) indicated 10 mg/l of styrene as lethal to fish and nekal as lethal to fish at 20 mg/l. Nekal is a linear detergent commonly used for the polymerization of co-polymer rubber. Mann (1964) determined that the tainting of fish by either phenol or oil refinery waste water was more pronounced in the presence of detergents. Thus, it may be that the emulsifying agents appearing in the co-polymer serum are accelerating and intensifying the tainting of the fish. While it is of lesser importance the discharge of rubber crumbs and low molecular weight polyisoprene results in a stickly, unsightly, seemingly indestructible accumulations along the river bank.

Table 4 contains 11 incidents in which the fish of station 4 were subjected to fluctuating pH levels. In reviewing the literature (E.I.F.A.C. 1969; Calabrese, 1969; Lloyd and Jordan, 1964; Jordan and Lloyd, 1964) it has been established that the pH range of 5-9 is not lethal to fish

although changes in acidity or alkalinity within this range may render some common pollutants lethal. Between pH levels of 4-5 and 9-10 some fish mortality can be expected while even brief exposures to pH below 4 and above 10 will produce almost instant death. An acid discharge may release sufficient CO_2 to be lethal within the pH range of 5-6.

CONCLUSION

As defined by the parameters of this study it has been found that the water of the upper St. Clair River at station 1 is capable of supporting fish which have good flavor and growth rate. The river water at this station is free of oily, petrochemical odours.

The river water at station 2 has become sufficiently contaminated to severly taint fish and stunt their growth. The river, covered with a chronic oil slick, smells of oil and reduced sulphur compounds.

The condition of the water at station 3 has shown some improvement over those conditions observed at station 2. However, there is still pronounced impairment of fish flavor and retardation of fish growth rates. The odour of the water at station 3 is similar to that of station 2.

Extreme pH fluctuations monitored at station 4 and coming from the 54-inch sewer constitue a major threat to aquatic life. Presently, the Polymer Corporation does not have adequate facilities for controlling the pH of this sewer. Both the raw fish and the river water smell of tertiary butyl alcohol. The cooked fish have a strong, oily flavor. The growth rate of fish at this station is considerably reduced from that of controls at station 1. The retardation of growth occurs independently of the pH fluctuations.

As a result of repeated lethal discharges coming from the 66-inch sewer it was not possible to keep fish alive at station 5 long enough for an assessment of the effects of these wastes on fish growth rate. There is inadequate capability within the plant to detect and contain these lethal discharges. Two types of taint were observed at station 5; one was of an oily, rubbery character, the other was of a reduced hydrocarbon character similar to styrene. The first type of taint was found in the fish after 23 days exposure. The second type of taint was acquired after approximately one hour exposure to styrene and ethyl benzene at approximately 36 ppm and 11 ppm respectively. The continued close co-operation of the Polymer Corporation Limited and the Ministry of the Environment is essential for the satisfactory resolution of the problems of lethal discharges and tainted fish.

RECOMMENDATIONS

1) Further steps must be taken within the Imperial Oil Enterprises Limited refining and petrochemical plant to control the discharge of non-volatile oil and other organic materials to the St. Clair River. Those substances and process wastes which are known to be toxic to fish, or to taint fish or water, should be removed from the waste streams discharged to the river.

2) The pH of the P.C.L. 54-inch sewer must be controlled to levels of pH 5.5 to pH 9.5.

3) The process waste of the P.C.L. 54-inch sewer must be treated to the point where it will no longer be toxic to fish or cause tainting.

4) More adequate measures must be taken within the P.C.L. plant to control and detect spills and slug discharges especially in those areas draining into the 66-inch sewer.

A sequential dissection of all sewer discharges should be completed by Polymer Corporation Limited. Such a dissection should include co-relational studies of COD, TOC, threshold odour, fish tainting and acute toxicity to fish. Two or more of these parameters used together would provide a means by which the simpler chemical and biological parameters could be used to detect the most noxious individual wastes. When the most toxic and/or taint-causing wastes have been identified, appropriate abatement programs should be applied to render these wastes compatible with the maintenance of a healthy, untainted aquatic fauna at the periphery of initial zones of dilution in the St. Clair River.

ACKNOWLEDGEMENTS

Special thanks to Mr. Harvey Minnis for his week-end coverage of the experiment, Mr. Ian Harris for his guidance and moral support and Mr. Bill Gunn for the willing assistance of his maintenance staff.

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A P P E N D I X I

Table 1: Polymer Corporation Limited. Operating units and typical waste water contaminants.

Operating Unit	Main Drainage Sewer Process Waste Water	Cooling Water	Contaminants in Process Waste Water
Butadiene Unit	66 (stn. 5)	Twp. Ditch (stn. 3)	Carbonyl solvents (acetone, methyl ethyl ketone) oils, acetonitrile, organo-copper, catalysts.
Latex Unit	66 (stn. 5)	Twp. Ditch (stn. 3)	Wastes handled by Co-poly Unit.
Feed preparation Unit	54 (stn. 4)		Acids alkalies tert butyl alcohol. Isobutylene dimer
Co-Polymer Unit	66 (stn. 5)	Twp. Ditch (stn. 3)	Sulphate, Sulphonates Styrene
Butyl Unit	66 (stn. 5)		Varsol Low moll. wt. isoprene
Styrene Unit	66 (stn. 5)		Styrene, benzene, ethyl-benzene, water extract of crude benzene, toluene
Stereo Unit	72 (stn. 5)		Benzene. Rubber crumb alkalis hexane.

Information supplied by P.C.L.

Table 2: Polymer Corporation Limited, Major Sewer Flows

SEWER FLOWS	
Township Ditch	40.5 M.I.G.P.D.
54 Inch Sewer	14.0 M.I.G.P.D.
66" Sewer	76.3 M.I.G.P.D.
72" Sewer	10.0 M.I.G.P.D.

Information supplied by P.C.L.

TABLE 3 — FISH ENUMERATION

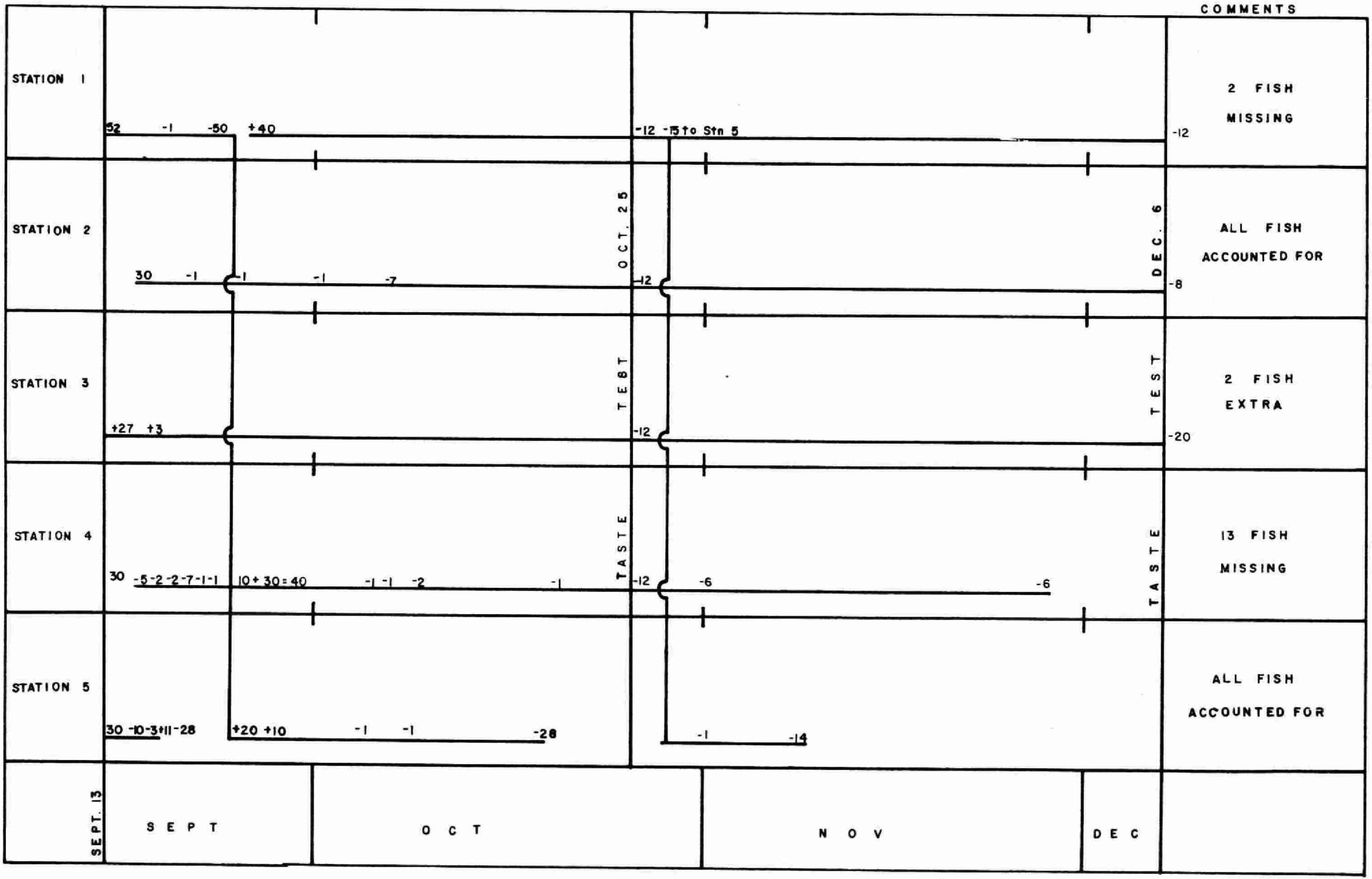

Table 4. Spills and Unusual Discharges

DATE	CONTAMINANT	AMOUNT OR DURATION	SOURCE SUSPECTED OR CONFIRMED	STATION AFFECTED
Sept.14	pH fluctuations	N.A.	Feed Prep area	4- Total fish kill
Sept.24	Low moll wt. isoprene	Estimated <50 I.G.	Butyl Unit	5- Mess on river bank
Sept.30	pH fluctuations	1.5 hrs.	Feed Prep area	4- Fish stunned but recovered
Oct. 1	Strong caustic	< 1 hour	Stereo Unit	5- No effect.
Oct. 1	pH fluctuations	2 hours	Feed Prep volt	4- Fish Tank pump turned off.
Oct.2	Hexane	17,000 Imp.gal.	Stereo Unit	5- Fish tank pump turned off.
Oct.3	pH fluctuations	1 hour	Feed prep unit	4- Fish stunned but recovered
Oct.6	pH fluctuations	1.5 hours	Feed Prep unit	4- Fish tank pump turned off
Oct. 14	Acetonitrile/oil emulsion	several hours	Butadiene Unit	5- Apparently no effect
Oct. 17	Water extract of crude benzene	< 1 hour	Styrene Unit	5- Total Fish kill
Oct. 22	pH fluctuations	14 hours	Feed prep unit	4- fish tank pump turned off
Oct. 30	pH fluctuations	1/2 hour	Feed prep Unit	4- Partial fish kill
Nov. 8	Mixture of styrene ethylbenzene benzene	< 1 hour	styrene Unit	5- No damage to float. Total fish kill

Table 4. Continued

DATE	CONTAMINANTS	AMOUNT DURATION	SOURCE SUSPECTED OR CONFIRMED	STATION AFFECTED
Nov.10	pH Fluctuation	< 1 hour	Feed prepunit	4- Fish apparently unaffected
Nov.12	pH Fluctuations	2.5 hours	Feed Prep Unit.	4- Fish unaffected repair work on pH controller
Nov.15	Carbon black	< 1 hour	Butadiene Unit	5 -
22	pH Fluctuations	1 hour	Feed Prep unit	4 - Fish tank pump turned off.
27	pH fluctuations	1.5 hours	Feed prep unit	4 - Total Fish kill.
Dec. 7	Styrene, ethylbenzene etc.	Several Hours	Styrene Unit	5- Partially melted plastic float in river Potentially lethal.

TABLE 5: Summary of Elementary Water Quality Parameters

STATION	Temperature °C		D.O. (mg/l)	% Saturation	pH
1	Max.	20	12.5	96.8	8.5
1	Min.	5	7.7	81.5	7.7
2	Max.	22	11.5	98.1	8.9
2	Min.	6	7.0	72.9	7.8
3	Max.	22	14.2	115.0	9.2
3	Min.	6	6.7	74.5	7.3
4	Max.	24	11.4	108.5	12.5
4	Min.	10	6.4	73.0	2.0
5	Max.	23	8.8	93.6	8.5
5	Min.	12	7.0	71.1	8.0

A P P E N D I X II

POLYMER CORPORATION LIMITED
Petrochemicals Division

TO: Mr. G.M. Hicks

FROM: H. Minnis

DATE: December 16, 1971

Fish Toxicity Tests

Effluent Dilutions at Fish Tank Inlets

Originally, it was intended to use 100:1 dilutions of our effluents for these tests. Subsequent measurements show the actual dilutions to be considerably smaller.

Quoted data is only approximate. Constantly changing flow patterns and problems in finding suitable parameters made it impractical to provide accurate dilution factors.

Polymer Pumphouse

Average dilution 5:1

Under most conditions the dilution would be no greater than 9:1.

Polymer Deck

Average dilution 2:1

Dilutions ranged from 1:1 to 4:1 and the measurements are considered fairly reliable.

South Tank

66" Outfall

Only two measurements were possible at this location.

(1) November 8th - The tank inlet was sampled at the time of the fish kill. Dilution between 5-6:1.

(2) November 18th - At this time the intake buoy was near the edge of the 66" plume and the dilution would be near to maximum. Dilution 10:1.

<u>72" Outfall</u>

Only one measurement was made at this location. Dilution between 8-12:1. At the time of measurement the 72" plume was barely reaching the buoy due to a back eddy current. Dilution would be expected to be about maximum.

H. Minnis

H. Minnis

HM:brh

c.c. A.S. Dunlop
I.W.E. Harris
G.K. McKee
W. Komarnicky
A.R. Powell
D.L. Wells (O.W.R.C.)
J. Newton

A P P E N D I X III

POLYMER CORPORATION LIMITED

FISH KILL INVESTIGATION

STATION 5

OCTOBER 17

POLYMER CORPORATION LIMITED

RISK CONTROL DIVISION

TO: File 2.2.1

FROM: I. W. E. Harris DATE: November 19, 1971

Investigation of Death of O.W.R.C.
Test Fish in the South Tank
October 17, 1971

Conditions:

Time and Date: between 1:00 p.m. and 5:00 p.m., October 17, 1971

Meteorology: Wind - S.E., 2 m.p.h. to N.E., 7 m.p.h.
Temperature - 60-65°F

Sky Cover: 0% overcast.

Unit Operations:

All units were operating within the normal range of performance except that the Styrene Unit was preparing to start up and Butadiene "A" Unit had just shut down.

Effects Observed:

The Polymer Security Patrol checked the fish in all the tanks at 1:00 p.m. and all were normal. At about 5:00 p.m. the routine check revealed that all fish in the south tank were dead. The fish in the other tanks were all normal. No unusual odour was noted in the shed housing the tank at the south end and the appearance of the water in the tank was normal. Some fish were floating belly up, others had sunk to the bottom. The river at 5:00 p.m. and previously that afternoon had been noted to be slightly more turbid than normal.

Action:

The Security Guard notified Harvey Minnis and he arrived at about 6:00 p.m. All fish in the south tank were checked and found to be dead. About six were removed from the tank, placed in a clean plastic bag and frozen in the Main Laboratory for possible autopsy.

The following water samples were taken:

(a) water from the south tank (6:00 p.m., October 17, 1971)

(b) composite from 72" sewer (6:00 p.m. to 9:00 a.m., Oct. 16-17/71)

(c) composite from 72" sewer (9:30 a.m. to 6:00 p.m., Oct. 17/71)

(d) composite from 66" sewer (6:00 p.m. to 9:00 a.m., Oct. 16-17/71)

(e) composite from 66" sewer (9:30 a.m. to 6:00 p.m., Oct. 17/71)

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(f) water in Styrene Unit, Tank 6 (Oct. 18/71)

(g) water in Styrene Unit, Tank 9 (Oct. 18/71)

(h) water in Styrene Unit, Tank 6 (Oct. 20/71)

(i) water in Styrene Unit, Tank 9 (Oct. 20/71)

The samples from the water in the Styrene Unit Tanks were taken because they were draining at the time of the fish kill.

Unit Pollution Control Coordinators on all units were questioned as to the operations underway on the weekend of October 16 and 17, 1971 so that deviations from the normal operations could be established.

The analyses on the above samples are as follows:

Identification	COD (ppm)	Phenolics (ppm)	pH	Other
(a) south tank water, Oct. 17/71	No analyses. Odour and appearance normal.			
(b) 72" composite, Oct. 16-17/71	12	--	8.2	--
(c) 72" composite, Oct. 17/71	28	--	7.9	--
(d) 66" composite, Oct. 16-17/71	60	--	8.8	Less than 10 ppm
(e) 66" composite, Oct. 17/71	60	0.038	8.8	Less than 10 ppm
(f) Tank 6, Oct. 18/71	--	--	5.9	Total Fe: 32 ppm Total S: 496 ppm Total N: 267 ppm
(g) Tank 9, Oct. 18/71	--	--	6.4	Total Fe: 34 ppm Total S: 229 ppm Total N: 190 ppm
(h) Tank 6, Oct. 20/71	--	--	5.2	Total Fe: --- Total S: 758 ppm Total N: 276 ppm
(i) Tank 9, Oct. 20/71	--	--	6.2	Total Fe: --- Total S: 205 ppm Total N: 174 ppm

Some crude fish toxicity tests were run on the water from tanks 6 and 9 taken on October 18, 1971. These tests indicated that the water from tank 6 was significantly more toxic than that from tank 9. However, at the dilutions to be expected in the fish tank, significant toxicity was not observed.

The water from both tanks 6 and 9 on October 19, 1971 were noted to contain more suspended solids than is usually found. The colour of the water on October 18, 1971 and at other times is very similar to that of light oil hence, visual identification is questionable.

The hydrocarbon gas detector in the 54" sewer at the Feed Preparation Unit (catchbasin at 20 + 80W, 3 + 20S) showed a spike to 100% of the explosive limit between 2:15 p.m. and 3:15 p.m. on October 17, 1971. This device has, in the past, been shown to be sensitive to explosive gas concentrations in the 66" sewer because of the cross-connection between the two systems at that point.

Conclusions:

The evidence from the investigations indicate the most probable cause of the fish kill on October 17, 1971 to be the discharge of a moderately volatile hydrocarbon (e.g. benzene) from the Styrene Unit during draining tank 6 or tank 9. An exposure of two hours of 60 p.p.m. benzene is capable of completely killing fish. Therefore, a lethal concentration in the fish tank could have been achieved if as little as 1000 U. S. gals. of light oil was discharged over a one hour period.

Although this conclusion is considered to be most probable, the data are insufficient to allocate to it a high degree of certainty.

Recommendations:

It is essential that:

(i) the explosive gas detector and alarm be relocated to monitor all water streams from the Styrene Unit and be provided with a recording device (seven day chart would be adequate).

(ii) the need for close supervision of the water draining from the light oil tanks be emphasized. The water level must be kept as high as possible to minimize the chance of over-draining the tank and discharging light oil.

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A P P E N D I X IV

APPENDIX IV

River Reach*	Percentage of Replys Indicating Unsatisfactory Water Quality		Percentage of Replys Indicating Adverse Effect on Water Use		Typical Complaints
I	100%	16/16	57%	9/16	odours, oil slicks discolouration, particles
II	89%	34/38	82%	31/38	oil slicks, odour discolouration
III	91%	30/33	61%	20/33	taste and odour in water, bacteriological contamination odour
IV	76%	22/29	45%	13/29	taste and odour in water discolouration odour, oil slicks.

* I - Chippewa Indian Reserve to Corunna
II - Corunna to Courtwright
III - Courtright to Sombra
IV - Sombra to Port Lambton.